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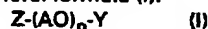
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(54) Curable emulsion containing a polymerizable silane and a polymerizable surfactant

(57) A curable emulsion is prepared by copolymerizing the following radical-polymerizable components (a) to (d) in the presence of a pH buffering agent in an aqueous medium: (a) an alkoxysilane containing a radical-polymerizable group; (b) a vinyl monomer copolymerizable with component (a); (c) the following (c-1) or (c-2): (c-1) being a polyester or a polyalkylene oxide having an average condensation degree of not less than 3 and having a radical-polymerizable group linked to one end of the molecule, the radical-polymerizable group being copolymerizable with component (a); and (c-2) being a macromonomer comprising a vinyl polymer or a polysiloxane having a radical-polymerizable group which is copolymerizable with component (a) and linked to one end of the vinyl polymer or polysiloxane molecule, the number average molecular weight of the macromonomer being 1,000 to 30,000; and (d) a radical-polymerizable anionic or cationic surfactant represented by the following general formula (I):



wherein Z represents a structural unit containing a radical-polymerizable group copolymerizable with component (a); AO represents an oxyalkylene group; n represents an integer of 2 or more; and Y represents an ion-dissociable group.

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CURABLE EMULSION AND COATING MATERIAL COMPRISING THE SAME

The present invention relates to a curable emulsion comprising a polymer containing an alkoxysilyl group, namely, a group in which a hydrolyzable alkoxy group links to a silicon atom. The curable emulsion is used for a paint or a coating agent.

Polymers prepared by copolymerizing a radical-polymerizable monomer containing an alkoxysilyl group, which is represented by γ -methacryloxypropyltriethoxysilane or vinyltriethoxysilane, with other monomers have been used for adhesives, sealing materials, paints, coating agents and the like. To avoid ill effects on human body and environmental pollution due to organic solvents used in these materials, aqueous type materials containing no organic solvents have been expected in recent years.

However, aqueous emulsions composed of polymers containing an alkoxysilyl group is disadvantageous in storage stability because the alkoxysilyl group inherently susceptible to hydrolysis. Many proposals for overcoming the disadvantage have been made.

That is, JP-A-3-227312 (The term "JP-A" as used herein means an "unexamined published Japanese patent

application") proposes that, in aqueous emulsion polymerization of an alkyl (meth)acrylate and a monomer containing an alkoxysilyl group, a specific water-soluble monomer such as acrylamide, acrylic acid and styrenesulfonic acid is copolymerized in an amount of from 0.1 to 5% by weight with the above-described monomers. Also, JP-A-5-25354 proposes a method comprising copolymerizing a monomer containing an alkoxysilyl group with a monomer containing an amineimido group in an alcohol solvent, adding water thereto to emulsify, and subsequently distilling the alcohol solvent to prepare an aqueous emulsion.

On the other hand, JP-A-59-152972 discloses that a specific amount of colloidal silica is blended in an aqueous emulsion prepared by aqueous emulsion polymerization of a vinylsilane, an acrylic monomer and a polymeric emulsifying agent to prepare an aqueous emulsion which forms a film excellent in water resistance.

However, known curable emulsions have disadvantages of being still insufficient in storage stability and of leaving a little more room for improvement in weather resistance and acid resistance of the resulting films.

The present inventors found that a radical-polymerizable alkoxysilane is copolymerized with another vinyl monomer in the presence of a pH buffering agent by use of an ionic surfactant containing both of a polyoxyalkylene

unit and a radical-polymerizable double bond to obtain a curable emulsion excellent in both the storage stability and physical properties of the resulting films, and applied for a patent on this invention (Japanese Patent Application No. 7-49129).

An object of the present invention is to provide a curable emulsion which has excellent storage stability and capable of forming a coating excellent in weather resistance and acid resistance.

Other objects and effects of the present invention will be more apparent from the following description.

After the above-described patent application, the present inventors further extensively studied curable emulsions. As a result, the present inventor found that an emulsion which forms a film more excellent in resistance to acid rain (hereinafter referred to as "acid resistance") and weather resistance, compared to the curable emulsion proposed in the above-described Japanese Patent Application No. 7-49129, is obtained by using:

an ionic surfactant which contains both a polyoxyalkylene unit and a radical-polymerizable double bond; and

a polyester or a polyalkylene oxide having an average condensation degree of not less than 3 and having a radical-

polymerizable group linked to one end of the molecule, or a macromonomer comprising a vinyl polymer or a polysiloxane having a radical-polymerizable group linked to one end of the vinyl polymer or polysiloxane molecule, the number average molecular weight of the macromonomer being 1,000 to 30,000; together with other monomers in polymerizing an alkoxysilane containing a radical-polymerizable group with other copolymerizable monomers in an aqueous medium. The present invention is based on the above described findings.

That is, the present invention has been achieved by providing a curable emulsion prepared by copolymerizing the following radical-polymerizable components (a) to (d) in the presence of a pH buffering agent in an aqueous medium:

(a) an alkoxysilane containing a radical-polymerizable group;

(b) a vinyl monomer copolymerizable with component (a);

(c) the following (c-1) or (c-2):

(c-1) being a polyester or a polyalkylene oxide having an average condensation degree of not less than 3 and having a radical-polymerizable group linked to one end of the molecule, the radical-polymerizable group being copolymerizable with component (a); and

(c-2) being a macromonomer comprising a vinyl polymer or a polysiloxane having a

radical-polymerizable group which is copolymerizable with component (a) and linked to one end of the vinyl polymer or polysiloxane molecule, the number average molecular weight of the macromonomer being 1,000 to 30,000; and

(d) a radical-polymerizable anionic or cationic surfactant represented by the following general formula (I):



wherein Z represents a structural unit containing a radical-polymerizable group copolymerizable with component (a); AO represents an oxyalkylene group; n represents an integer of 2 or more; and Y represents an ion-dissociable group.

The present invention is described in detail below.

Component (a) in the present invention is an alkoxysilane containing a radical-polymerizable group (hereinafter referred as to "alkoxysilane monomer") as described above. Examples thereof include vinyltrimethoxysilane, vinylmethyldimethoxysilane, γ -methacryloxypropyltrimethoxysilane, γ -methacryloxypropylmethyldimethoxysilane, vinyltriethoxysilane, vinylmethyldiethoxysilane, γ -methacryloxypropyltriethoxysilane,

γ -methacryloxypropylmethyldiethoxysilane,
vinyltripropoxysilane, vinylmethyldipropoxysilane,
 γ -methacryloxypropyltripropoxysilane and
 γ -methacryloxypropylmethyldipropoxysilane.

Of these, preferred are those having a methoxy or ethoxy group as the alkoxy group.

Examples of vinyl monomer (b) copolymerizable with the above-described component (a) include alkyl (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, cyclohexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate and stearyl (meth)acrylate; (meth)acrylic esters such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, perfluoroalkyl (meth)acrylates, glycidyl (meth)acrylate and N,N-diethylaminoethyl (meth)acrylate; vinyl acetate; vinyl propionate; styrene; and α -methylstyrene.

Of these, monomers which impart film-forming properties to the resulting polymers are preferred, and examples thereof include alkyl (meth)acrylates which have an alkyl group having from 1 to 8 carbon atoms, styrene, hydroxyalkyl (meth)acrylates which have a hydroxyalkyl group having from 2 to 3 carbon atoms, and glycidyl (meth)acrylate. These monomers may be used alone or in combination of two or more kinds thereof.

It is preferred to avoid using acidic monomers such as (meth)acrylic acid as component (b) because these compounds promote hydrolysis of the alkoxyethyl group.

Component (c) in the present invention is (c-1) or (c-2) as described above, that is,

(c-1): a polyester or a polyalkylene oxide having an average condensation degree of not less than 3 and having a radical-polymerizable group linked to one end of the molecule, the group being copolymerizable with the above-described component (a) (Hereinafter referred to as a "polyester monomer" and a "polyalkylene oxide monomer", respectively); or

(c-2): a macromonomer comprising a vinyl polymer or a polysiloxane having a radical-polymerizable group which is copolymerizable with component (a) and linked to one end of the vinyl polymer or polysiloxane molecule, the number average molecular weight of the macromonomer being 1,000 to 30,000.

The radical-polymerizable group in components (c-1) and (c-2) is preferably a (meth)acryloyl group.

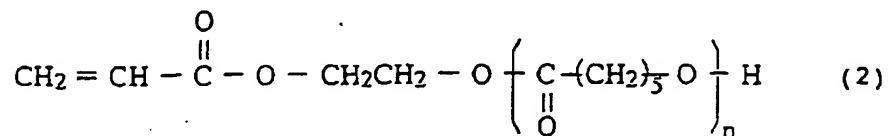
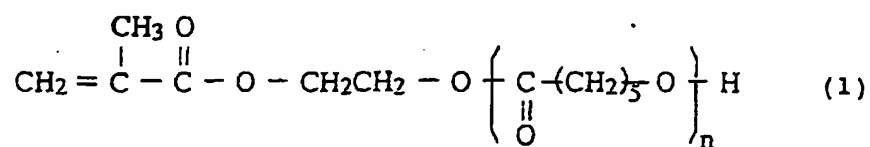
Component (c-1) is described in detail below.

Preferred monomer unit for forming the polyester moiety of the polyester monomer includes oxycarboxylic acids and lactones, and the average condensation degree of the polyester moiety is preferably from 3 to 100, more preferably

from 3 to 8. Preferred monomer unit for forming the polyalkylene oxide moiety of the polyalkylene oxide monomer includes ethylene oxide and propylene oxide, and the average condensation degree of the polyalkylene oxide is preferably from 3 to 200.

When the condensation degree of the respective monomer unit for forming the polyester monomer or the polyalkylene oxide monomer is not more than 2, the resulting curable emulsion fails to form a film excellent in acid resistance.

Particularly preferred examples of component (c-1) in the present invention include polyester monomers comprising polycaprolactones having an average condensation degree of from 3 to 8, which are represented by the following formulas (1) or (2):



Commercially available polyester monomers may be used as the polyester monomer. Examples thereof include Placel FM3 (a compound represented by formula (1), $n=3$), Placel FA3 (a compound represented by formula (2), $n=3$), Placel FM6 (a compound represented by formula (1), $n=6$), Placel FA6 (a compound represented by formula (2), $n=6$), Placel FM8 (a compound represented by formula (1), $n=8$) and Placel FA8 (a compound represented by formula (2), $n=8$), each manufactured by Daicel Chemical Industries, Ltd.

Examples of the polyalkylene oxide monomer include Blemmer PP-1000 (polypropylene oxide which has a methacryloyl group linked to one end of the molecule and has a condensation degree of from 5 to 6), Blemmer PP-500 (polypropylene oxide which has a methacryloyl group linked to one end of the molecule and has a condensation degree of 9), Blemmer PP-800 (polypropylene oxide which has a methacryloyl group linked to one end of the molecule and has a condensation degree of 12), Blemmer PE-200 (polyethylene oxide which has a methacryloyl group linked to one end of the molecule and has a condensation degree of from 4 to 5), and Blemmer PE-350 (polyethylene oxide which has a methacryloyl group linked to one end of the molecule and has a condensation degree of from 7 to 9), each manufactured by Nippon Oil and Fats Co., Ltd.

Macromonomer (c-2) is described in detail below.

If the number average molecular weight of macromonomer (c-2) is less than 1,000, acid resistance thereof is deteriorated, whereas if the number average molecular weight exceeding 30,000, copolymerizability thereof with other polymerizable components is deteriorated. The number average molecular weights used in the present invention are those obtained by gel permeation chromatography in terms of the polystyrene conversion.

Preferred vinyl polymers used as structural unit of macromonomer (c-2) include homopolymers or copolymers of alkyl (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate and n-butyl (meth)acrylate, and homopolymers or copolymers of 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, acrylonitrile, vinyl acetate, styrene and the like.

In the present invention, either of the above-described vinyl polymers and polysiloxanes can be used as the polymer skeleton of the macromonomer. However, the above-described vinyl polymers are preferably used because a coating film formed from the resulting curable emulsion exhibits excellent transparency.

Examples of macromonomer (c-2) are given below.

These macromonomers each contains a methacryloyl group as the radical-polymerizable group.

Macromonomers Manufactured by Toagosei Chemical Industry Co.,
Ltd.:

LS-6 (polystyrene, the number average molecular weight: 6,000)

AN-6 (copoly(styrene/acrylonitrile), the number average molecular weight: 6,000)

AA-6 (poly(methyl methacrylate), the number average molecular weight: 6,000)

AA714S (copoly(methyl methacrylate/2-hydroxyethyl methacrylate), the number average molecular weight: 7,000)

AX707S (copoly(butyl methacrylate/2-hydroxyethyl methacrylate), the number average molecular weight: 7,000)

AK5 (polysiloxane, the number average molecular weight: 5,000)

AK30 (polysiloxane, the number average molecular weight: 30,000)

Macromonomer Manufactured by Chisso Corp.:

FM0725 (polysiloxane, the number average molecular weight: 10,000).

Component (d) in the present invention is a radical-polymerizable anionic or cationic surfactant containing both a polyoxyalkylene group and an ion-dissociable group, the surfactant being represented by the following general formula (I):



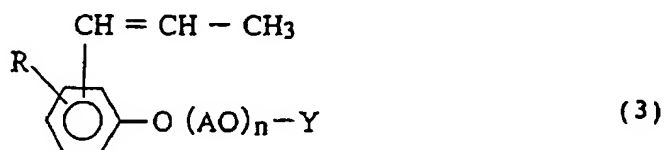
wherein Z represented a structural unit containing a radical-polymerizable group copolymerizable with the above-described component (a); AO represents an oxyalkylene group; n represents an integer of not less than 2; and Y represents an ion-dissociable group.

Z in the above-described general formula (I) is preferably a structural unit in which a hydrophobic group such as an aromatic hydrocarbon group, an alkyl-substituted aromatic hydrocarbon group, a higher alkyl group and a heterocyclic hydrocarbon group is combined with a radical-polymerizable group. The radical-polymerizable group in Z is preferably a (meth)allyl group, a propenyl group or a butenyl group.

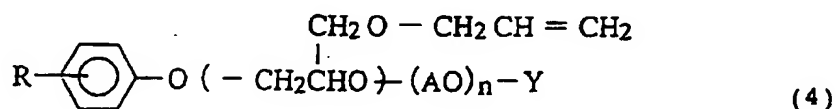
The ionicity of component (d) is preferably an anion, and examples of preferred Y include $-\text{SO}_3\text{Na}$, $-\text{SO}_3\text{NH}_4$, $-\text{COONa}$, $-\text{COONH}_4$, $-\text{PO}_3\text{Na}_2$ and $-\text{PO}_3(\text{NH}_4)_2$. Of these, $-\text{SO}_3\text{Na}$ and $-\text{SO}_3\text{NH}_4$ are more preferred.

Subscript n in the $(\text{AO})_n$ group is preferably not more than 300, and more preferably from 5 to 50. If n is less than 5, stability of the alkoxysilyl group in the above-described monomer (a) is apt to be insufficient, whereas if n exceeds 50, physical properties of a film formed from the resulting curable emulsion is lowered. The structural unit A in the $(\text{AO})_n$ group, namely, an alkylene group is preferably an ethylene group or a propylene group.

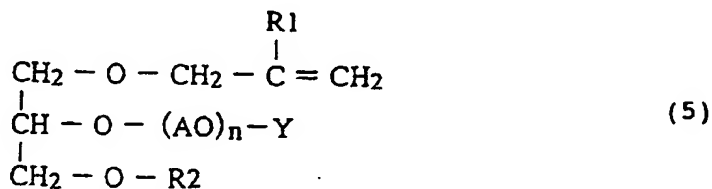
Typical examples of the above-described radical-polymerizable surfactant (d) include compounds represented by formulas (3), (4) and (5). In each formula, Y represents an ion-dissociable group, and preferred examples thereof are described above.



wherein R is preferably a straight- or branched-chain alkyl group having from 6 to 18 carbon atoms.



wherein R is preferably a straight- or branched-chain alkyl group having from 6 to 18 carbon atoms.



wherein R1 represents a hydrogen atom or a methyl group, and R2 is preferably an alkyl group having from 8 to 24 carbon atoms.

In the present invention, when the above-described radical-polymerizable components (a) to (d) are polymerized in an aqueous medium such as water, a pH buffering agent is used to stabilize the alkoxysilyl group of component (a). Buffering agents suitable for maintaining the aqueous medium to have a pH of from 6 to 10 are preferably used in the present invention. Examples of such pH buffering agents include sodium hydrogencarbonate, potassium hydrogencarbonate, monosodium phosphate, monopotassium phosphate, disodium phosphate, trisodium phosphate, sodium acetate, ammonium acetate and sodium formate. These compounds may also be used in combination of two or more kinds thereof.

A more preferred pH buffering agent is sodium hydrogencarbonate because it can stabilize pH by addition of a small amount thereof.

The amount of the pH buffering agent used is preferably from 0.01 to 5% by weight based on the weight of the aqueous medium.

Proportions of the above-described radical-polymerizable components (a) to (d) to the total amounts thereof are preferably from 1 to 40% by weight for component (a), from 50 to 97% by weight for component (b), from 1 to 40% by weight for component (c), and from 0.2 to 20% by weight for component (d), and more preferably from 3 to 20%

by weight for component (a), from 50 to 93% for component (b), from 3 to 30% by weight for component (c), and from 0.5 to 5% by weight for component (d).

When the proportion of component (a) is less than 1% by weight, the resulting curable emulsion fails to exhibit adequate curable properties. On the other hand, when the proportion thereof exceeds 40% by weight, storage stability of the resulting curable emulsion tends to be deteriorated. When the proportion of component (c) is less than 1% by weight, acid resistance of a film formed from the resulting curable emulsion is deteriorated, whereas when the proportion exceeds 40% by weight, weather resistance of the resulting film tends to be deteriorated. When the proportion of component (d) is less than 0.2% by weight, polymerization stability is lowered, whereas when the proportion exceeds 20% by weight, water resistance of the resulting film is insufficient. When the proportion of component (b) is less than 50% by weight, film-forming properties of the resulting curable emulsion and adhesion property of the resulting film to a substrate are deteriorated.

Subsequently, the polymerization process for use in the present invention is described below.

In the present invention, the above-described components are preferably copolymerized by a microsuspension polymerization process using an oil-soluble polymerization

initiator to efficiently copolymerize macromonomer (c) with other components.

To carry out the microsuspension polymerization, finely divided particles composed of the monomer components (a) to (c) and the oil-soluble polymerization initiator are dispersed into an aqueous medium in which a pH buffering agent is dissolved. It is preferred that the above-described surfactant (d) is previously dissolved in the aqueous medium as well as the pH buffering agent prior to dispersion of the monomer components (a) to (c) into the aqueous medium. The amount of the aqueous medium is suitably about from 20 to 150 parts by weight per 100 parts by weight of the monomer components.

A dispersing process using a rotating homomixer, a high-pressure type emulsifier (usually referred to as a "homogenizer"), a turbine type mixer, or the like can be applied to the dispersion of the above-described finely divided particles into the aqueous medium.

Finely divided particles having a diameter of not more than 1 μm can be obtained by the above-described operation. The smaller the dispersed particles of the monomers are, the smaller the obtained polymer particles in the polymer emulsion become. Further, a film formed from such an emulsion exhibits excellent solvent resistance and

water resistance. More preferred particle sizes are from 0.05 to 0.2 μm .

The thus prepared aqueous dispersion of the finely divided particles (hereinafter referred to as a "monomer emulsion") comprising the monomers and the oil-soluble polymerization initiator is fed to an aqueous medium, such as water, heated above the decomposition temperature of the polymerization initiator, thus components (a) to (d) being allowed to copolymerize. Preferred amount of the aqueous medium charged previously in a polymerization vessel is from 10 to 50 parts by weight per 100 parts by weight of the monomer emulsion. The polymerization temperature is generally about from 40 to 100°C, and preferably from 70 to 90°C.

The oil-soluble radical polymerization initiator for use in the microsuspension polymerization preferably have a solubility of not more than 10% by weight in water at 20°C, and typical examples thereof include azo type initiators such as 2,2'-azobisisobutyronitrile, 2,2'-azobis-2,4-dimethylvaleronitrile, 1,1'-azobis-(cyclohexane-1-carbonitrile) and dimethyl 2,2'-azobisisobutyrate; and organic peroxides such as lauroyl peroxide, benzoyl peroxide, dicumyl peroxide, cyclohexanone peroxide, di-n-propyl peroxydicarbonate and t-butyl peroxyphthalate. The amount of the oil-soluble radical polymerization initiator used in the polymerization

is preferably from 0.1 to 10% by weight, and more preferably from 0.5 to 5% by weight based on the total weight of components (a) to (d).

Further, when (c-1) is used as component (c), the curable emulsion of the present invention is preferably prepared also by a known emulsion polymerization process using a known emulsifier, for example, polymerizing monomers by the action of an aqueous polymerization initiator in a micelle formed by an emulsifier.

The curable emulsion of the present invention which are prepared by the above-described microsuspension polymerization or emulsion polymerization can stay as a stable emulsion state and retain good curing performance even after storage for one month at 60°.

The curable emulsion of the present invention is suitably used as a coating material, and examples of coated materials include metallic base materials such as iron, stainless steel, tinplate, aluminum and nickel; cement type base materials such as concrete, slates, mortar, calcium silicate materials and gypsum/slag materials; resin-molded materials formed from an acrylic resin, a vinyl chloride resin, a polyester resin, a polycarbonate resin, ABS, Bakelite, a nylon or an epoxy resin; glass; woods such as cedar and the Japanese cypress; and paper.

Prior to use of the curable emulsion as a coating material such as paint, a catalyst can be preferably added to the emulsion to promote a condensation reaction of silanol groups formed by hydrolysis of the alkoxysilyl groups. Examples of the catalyst include organic titanate compounds such as isopropyltriisostearoyl titanate and isopropyltri(dioctyl pyrophosphate) titanate; organotin compounds such as dibutyl tin dioctylate, dibutyl tin dilaurate and dibutyl tin maleate; and organic acids such as p-toluenesulfonic acid.

The coated film can be cured by drying at ordinary temperatures or by drying with heating, and preferred drying conditions are as follows; from 3 to 14 days at ordinary temperatures or about 3 to 30 minutes at a temperature of from 100 to 150°C.

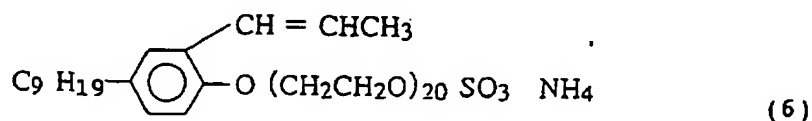
When the curable emulsion is used as a paint, a thickening agent, a film-forming additive and a pigment may also be used in combination, and further coating additives such as an anti-sagging agent, an anti-setting additive, an anti-foaming agent and a silane coupling agent may also be added to the emulsion, as needed. Examples of the coating method of the curable emulsion of the present invention include spray coating, roller coating and brush coating.

In addition to the above-described uses, the curable emulsion of the present invention is used as a water

repellant for inorganic building materials, a moisture-resistant coating agent for electronic parts, a back coating agent for magnetic tapes, a hardening finish for fabrics, a sealing agent, an adhesive, a binder, a pressure-sensitive adhesive or the like.

The present invention will be describe in more detail below with reference to Examples and comparative Examples, but the invention should not be construed as being limited thereto. All "part" indicating a content in the respective examples are by weight unless otherwise indicated.

Aqualon HS20 (trade name, manufactured by Dai-ichi Kogyo Seiyaku Co., Ltd.) used as a radical-polymerizable surfactant is a compound represented by the following formula (6).



Curable emulsions prepared in the respective examples were each applied to an aluminum plate with a bar coater so as to be 20 to 25 μm in film thickness, and dried for 14 days at a temperature of 25°C and humidity of 60% to prepare test pieces for evaluating the following physical properties of the resulting coated film.

a) Water Resistance

The above test pieces were immersed in ion-exchanged water and then stored at 25°C for 7 days to observe a whitening degree of the film. Criteria of the evaluation are as follows:

- o: No changes were observed;
- Δ: Somewhat whitened; and
- x: Completely whitened.

b) Acid Resistance

One drop of 5% sulfuric acid was placed on the respective films, and then allowed to stand at 60°C for 10 minutes to evaluate states of the films. Criteria of the evaluation are as follows:

- o: No changes were observed;
- Δ: A mark was observed; and
- x: The film was loosened or peeled.

c) Accelerated Weathering Test

The films were deteriorated according to the method specified by JIS K5400 by a Sunshine Weather Meter manufactured by Suga Test Instruments Co., Ltd. to evaluate the weather resistance in terms of the gloss retention (%) of gloss (60°) after the elapse of 3,000 hours to initial gloss (60°).

EXAMPLE 1

Monomers, a radical-polymerizable surfactant and a polymerization initiator shown in Table 1 below were added to

an aqueous medium in which a pH buffering agent had been dissolved, mixed with a homomixer and then further mixed by a homogenizer (manufactured by Gaulin Co.) to prepare a monomer emulsion having a pH of 8.5 and an average particle size of 0.2 μm .

In a flask equipped with a stirrer, a thermometer and a condenser, 40 parts of deionized water was placed, and the temperature of the aqueous medium was raised to 80°C. The above-described monomer emulsion was then added dropwise to the aqueous medium over a period of 2 hours with stirring at high speed. After completion of the addition, the reaction mixture was maintained at 80°C for 2 hours to accomplish polymerization, and then cooled to room temperature. Although slight amount of aggregates attached to the inner wall of the flask during the polymerization, the polymerization was stably carried out without liquid separation and blocking. Results of the evaluation of the physical properties of the film formed from the resulting curable emulsion are shown in Table 3.

TABLE 1

<u>Composition</u>	<u>Components</u>	<u>Content (part)</u>
Monomer (a)	γ -Methacryloxypropyltriethoxysilane	10
Monomer (b)	Methyl Methacrylate	50
	n-Butyl Acrylate	25
	2-Hydroxyethyl Methacrylate	5

Monomer (c)	Placel FM6	10
Surfactant (d)	Aqualon HS20	2
Polymerization Initiator	2,2'-Azobisisobutyronitrile	1
pH Buffering Agent	Sodium hydrogencarbonate	0.2
Aqueous Medium	Deionized Water	100

EXAMPLES 2 TO 4

Curable emulsions were prepared in the same manner as in Example 1, except that monomers and a radical-polymerizable surfactant shown in Table 2 were used each in the amount shown therein, respectively. Results of the evaluation of the physical properties of the films formed from the resulting emulsions are shown in Table 3.

COMPARATIVE EXAMPLES 1 TO 3

Curable emulsions were prepared in the same manner as in Example 1, except that monomers and a radical-polymerizable surfactant shown in Table 2 were used each in the amount shown therein, respectively. In comparative Example 2, Placel FM1, which is represented by formula (1) wherein $n=1$, was used as component (c) in place of Placel FM6 used in Example 1. Further, in comparative Example 3, two parts of a surfactant containing no radical-polymerizable group, Levenol W2 (trade name, polyoxyethylene alkyl phenyl ether sulfuric ester salt, manufactured by Kao Corp.), was

used in place of the radical-polymerizable surfactant used in Example 1.

Results of the evaluation of the physical properties of the films formed from the resulting curable emulsions are shown in Table 3.

TABLE 2

Components	Examples				Comparative Examples		
	1 (part)	2 (part)	3 (part)	4 (part)	1 (part)	2 (part)	3 (part)
(a) γ -Methacryloxypropyltriethoxysilane	10	10	10	10	10	10	10
(b) Methyl Methacrylate	50	50	50	50	50	50	50
n-Butyl Acrylate	25	30	25	25	35	25	25
2-Hydroxyethyl Methacrylate	5	5	5	5	5	5	5
(c) Placel FM1	-	-	-	-	-	10	-
Placel FM3	-	-	10	-	-	-	-
Placel FM6	10	5	-	-	-	-	10
Blenmer PP800	-	-	-	10	-	-	-
(d) Aqualon HS20	2	2	2	2	2	2	-

TABLE 3

<u>Example No.</u>	<u>Water Resistance</u>	<u>Weather Resistance (%)</u>	<u>Acid Resistance</u>
Example 1	o	92	o
Example 2	o	88	o
Example 3	o	91	o
Example 4	o	85	o
Comparative Example 1	o	55	x
Comparative Example 2	o	61	x
Comparative Example 3	x	75	Δ

EXAMPLE 5

Monomers, a radical-polymerizable surfactant and a polymerization initiator shown below were added to an aqueous medium in which a pH buffering agent had been dissolved, and mixed with a homomixer, and then further mixed by a homogenizer (manufactured by Gaulin Co.) to prepare a monomer emulsion having a pH of 8.5 and an average particle size of 0.2 μ m.

<u>Used Compounds</u>	<u>(Part)</u>
Component (a):	
γ -Methacryloxypropyltriethoxysilane	10
Component (b):	
Methyl Methacrylate	50
n-Butyl Acrylate	30

2-Hydroxyethyl Methacrylate	5
Component (c):	
AA-6 (manufactured by Toagosei Co., Ltd., Poly(Methyl Methacrylate) Type Macromonomer; Number Average Molecular Weight: 6,000)	5
Component (d):	
Aqualon HS20	2
Polymerization Initiator:	
2,2'-Azobisisobutyronitrile	1
pH Buffering Agent:	
Sodium Hydrogencarbonate	0.2
Aqueous Medium:	
Deionized Water	100

In a flask equipped with a stirrer, a thermometer and a condenser, 40 parts of deionized water was placed, and the temperature of the aqueous medium was raised to 80°C. The above-described monomer emulsion was then added dropwise to the aqueous medium over a period of 2 hours with stirring at high speed. After completion of the addition, the reaction mixture was maintained at 80°C for 2 hours to accomplish polymerization, and then cooled to room temperature.

Although slight amount of aggregates attached to the inner wall of the flask during the polymerization, the polymerization was stably carried out without liquid separation and blocking. Results of the evaluation of the

physical properties of the film formed from the resulting curable emulsion are shown in Table 5.

EXAMPLES 6 TO 9

Curable emulsions were prepared in the same manner as in Example 5, except that monomers and a radical-polymerizable surfactant shown in Table 4 were used each in the amount shown therein, respectively. Results of the evaluation of the physical properties of the films formed from the resulting emulsions are shown in Table 5.

COMPARATIVE EXAMPLE 4 AND 5

Curable emulsions were prepared in the same manner as in Example 5, except that monomers and a radical-polymerizable surfactant shown in Table 4 were used each in the amount shown therein, respectively. In comparative Example 5, two parts of a surfactant containing no radical-polymerizable group, Levenol WZ (trade name, polyoxyethylene alkyl phenyl ether sulfuric ester salt, manufactured by Kao Corp.) was used in place of the radical-polymerizable surfactant used in Example 5.

Results of the evaluation of the physical properties of the films formed from the resulting curable emulsions are shown in Table 5.

TABLE 4

Components	Examples					Comparative	
	5	6	7	8	9	4	5
	(part)	(part)	(part)	(part)	(part)	(part)	(part)
(a) γ -methacryloxypropyltriethoxysilane	10	10	10	10	10	10	10
(b) Methyl Methacrylate	50	50	50	50	50	50	50
n-Butyl Methacrylate	30	5	25	25	25	35	25
2-Hydroxyethyl Methacrylate	5	5	5	5	5	5	5
(c) AA-6	5	30	-	-	-	-	-
AA-714S	-	-	10	-	-	-	10
AK30	-	-	-	10	-	-	-
FM0725	-	-	-	-	10	-	-
(d) Aqualon HS20	2	2	2	2	2	2	2*

In the table, AA-714S and AK30 are macromonomers having the following structures, respectively, which are manufactured by Toagosei Co., Ltd.

AA-714S: copoly(methyl methacrylate/2-hydroxyethyl methacrylate) type macromonomer ($M_n = 7,000$).

AK30: polysiloxane type macromonomer ($M_n = 30,000$).

FM0725 is a polysiloxane type monomer ($M_n = 10,000$) manufactured by Chisso Corp. Levenol WZ was used in place of Aqualon HS20.

TABLE 5

<u>Example No.</u>	<u>Water Resistance</u>	<u>Acid Resistance</u>	<u>Weather Resistance</u> (%)
Example 5	o	o	85
Example 6	o	o	80
Example 7	o	o	86
Example 8	-*	o	91
Example 9	-*	o	93
Comparative Example 4	o	x	55
Comparative Example 5	x	Δ	71

* Dried coated films were too white and opaque to evaluate water resistance thereof.

The curable emulsion of the present invention has excellent storage stability, and in addition, a film having excellent acid resistance and weather resistance can be formed from the emulsion.

CLAIMS

1. A curable emulsion prepared by copolymerizing the following radical-polymerizable components (a) to (d) in the presence of a pH buffering agent in an aqueous medium:

(a) an alkoxysilane containing a radical-polymerizable group;

(b) a vinyl monomer copolymerizable with component (a);

(c) the following (c-1) or (c-2):

(c-1) being a polyester or a polyalkylene oxide having an average condensation degree of not less than 3 and having a radical-polymerizable group linked to one end of the molecule, the radical-polymerizable group being copolymerizable with component (a); and

(c-2) being a macromonomer comprising a vinyl polymer or a polysiloxane having a radical-polymerizable group which is copolymerizable with component (a) and linked to one end of the vinyl polymer or polysiloxane molecule, the number average molecular weight of the macromonomer being 1,000 to 30,000; and

(d) a radical-polymerizable anionic or cationic surfactant represented by the following general formula (I):



wherein Z represents a structural unit containing a radical-

polymerizable group copolymerizable with component (a); AO represents an oxyalkylene group; n represents an integer of 2 or more; and Y represents an ion-dissociable group.

2. The curable emulsion as claimed in claim 1, comprising 1 to 40% by weight of component (a), 50 to 97% by weight of component (b), 1 to 40% by weight of component (c) and 0.2 to 20% by weight of component (d) in terms of the copolymerization proportion based on the total weight of the curable emulsion.

3. The curable emulsion as claimed in claim 1, wherein component (b) is at least one monomer selected from the group consisting of alkyl (meth)acrylates having from 1 to 8 carbon atoms, styrene, hydroxyalkyl (meth)acrylates having a hydroxyalkyl group having from 2 to 3 carbon atoms, and glycidyl (meth)acrylate.

4. The curable emulsion as claimed in claim 1, wherein component (c) is (c-1) and the copolymerization of components (a) to (d) is carried out by a microsuspension polymerization process or an emulsion polymerization process.

5. The curable emulsion as claimed in claim 1, wherein component (c) is (c-2) and the copolymerization of components (a) to (d) is carried out by a microsuspension polymerization process.

6. A coating material comprising a curable emulsion obtained by copolymerizing the following radical-

polymerizable components (a) to (d) in the presence of a pH buffering agent in an aqueous medium:

(a) an alkoxysilane containing a radical-polymerizable group;

(b) a vinyl monomer copolymerizable with component (a);

(c) the following (c-1) or (c-2):

(c-1) being a polyester or a polyalkylene oxide having an average condensation degree of not less than 3 and having a radical-polymerizable group linked to one end of the molecule, the radical-polymerizable group being copolymerizable with component (a); and

(c-2) being a macromonomer comprising a vinyl polymer or polysiloxane having a radical-polymerizable group which is copolymerizable with component (a) and linked to one end of the vinyl polymer or polysiloxane molecule, the number average molecular weight thereof being 1,000 to 30,000 ; and

(d) a radical-polymerizable anionic or cationic surfactant represented by the following general formula (I):



wherein Z represents a structural unit containing a radical-polymerizable group copolymerizable with component (a); AO

represents an oxyalkylene group; n represents an integer of 2 or more; and Y represents an ion-dissociable group.



Application No: GB 9615475.2
Claims searched: 1-6

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Date of search: 21 October 1996

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:	
UK Cl (Ed.O):	C3P PFEK, PFEZ
Int Cl (Ed.6):	C08F 212/14, 220/10, 220/12, 220/14, 230/08
Other:	Online databases: WPI, CLAIMS

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	GB 2221689 (KANSAI) see Claims 1, 6 & 7; Examples 7 & 8	
A	GB 2192400 (KANSAI) see Claim 1 and Examples	
A, P	EP 0690109 A1 (NATIONAL STARCH) see Claim 1	
A	EP 0159894 A2 (CHISSO) see Claim 1	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.